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SYNTHESIS OF 2-HETEROBICYCLO[3.2.1]OCTANES AND THE CORRESPONDING MONOENES AND DIENES

PAUL BARRACLOUGH, SEVIM BILGIC and DOUGLAS W. YOUNG*
School of Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, England

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Abstract—Synthesis of the theoretically interesting 2-heterobicyclo[3.2.1.]octa-3,6-dienes and their dihydro-and tetrahydro-derivatives has been achieved in the oxygen, nitrogen and sulphur series. The parent compound of the nitrogen series appears to exist as 2-azabicyclo[3.2.1]octa-2, 6-diene rather than as the enamine (3, R=H). The Cope rearrangement equilibrium (2, X=NR)$\rightleftharpoons$(3) lies more to the side of the diene 3 when nitrogen is substituted with an electron withdrawing group than when an alkyl substituent is present. These effects seem to suggest no special bishomoconjugative stabilisation in the dienes 3.

In connection with our interest in 2-heterobicyclo[3.2.1]octa-3, 6-dienes as neutral bishomo-$(4n+2)$ π-electron systems,[1] we have synthesised a variety of these dienes and the corresponding dihydro-and tetrahydro-derivatives.

In the oxygen series, 2-oxabicyclo[3.2.1]octa-3, 6-diene(1) is well known[2] and has been shown to exist in equilibrium with *endo*-6-formylbicyclo[3.1.0]hex-2-ene (2, X=O) through a Cope rearrangement.[2] The related monoene, 2-oxabicyclo[3.2.1]oct-3-ene has also been prepared.[3] In the aza-series, 2-azabicyclo[3.2.1]octa-3, 6-dienes (3) substituted with an electron-withdrawing group on nitrogen are well-known and stable and there has been no evidence reported for these being in equilibrium with the imine Cope rearranged products (2, X=NR). The first task in preparing compounds for our study of homoconjugative effects was to prepare the reduced derivatives of these compounds.

N-Phenylsulphonyl-2-azabicyclo[3.2.1]octa-3, 6-diene (3, R=SO$_2$Ph) was prepared by the method of Oehlschlager and Zalkow[4] and had the expected spectral characteristics although spin decoupling experiments† caused us to revise the original assignments[4] to H$_6$ and H$_7$ in this compound and, by inference, to other 2-heterobicyclo[3.2.1]octa-3, 6-dienes.

When N-phenylsulphonyl-2-azabicyclo[3.2.1]octa-3, 6-diene (3, R=SO$_2$Ph) was reduced with LiAlH$_4$ in refluxing tetrahydrofuran, a major product, C$_{13}$H$_{15}$NO$_2$S was isolated. This had a ^{1}H NMR spectrum compatible with assignment of the structure as N-phenylsulphonyl-*endo*-6-aminomethylbicyclo[3.2.1]hex-2-ene (4). The spectrum was complicated by protons H$_7$ being diastereotopic and appearing as part of an ABX system but analysis was simplified by preparation of (7RS) $[7\text{-}^2H_1]$-N-benzenesulphonyl-*endo*-6-aminomethylbicyclo-[3.2.1]hex-2-ene by reduction of the diene 3 R=SO$_2$Ph with LiAlD$_4$. In the ^{1}H NMR spectrum of this compound the protons H$_7$ appeared as a pair of doublets. The structure 4 suggested for the reduction product was finally confirmed by an unambiguous synthesis from the known[5] carboxylic acid (5, R=OH). This was converted to the amide (5, R=NH$_2$) and thence reduced and treated with phenylsulphonyl chloride to yield the sulphonamide (4) identical in all respects with the product of LiAlH$_4$ reduction of the sulphonamide (3, R=SO$_2$Ph).

Although there was no spectral evidence for the co-existence of the sulphonamide (3, R=SO$_2$Ph) with its Cope rearrangement product (2, X=NSO$_2$Ph), it is evident that the product 4 of LAH reduction must have derived from the imine tautomer (2, X=NSO$_2$Ph). When the crude product from this reduction was reinvestigated, the ^{1}H NMR spectrum was consistent with its being comprised of a mixture of the sulphonamide (4) and 2-azabicyclo[3.2.1]oct-6-ene(6, R=H). This latter compound was a potentially useful synthon for the series of Δ^6-monoenes (6) and so it was of interest to optimise its yield. The Cope rearrangement leading to the sulphonamide (4) was likely to be preferred at higher temperatures and so the reduction of N-phenylsulphonyl-2-azabicyclo[3.2.1]octa-3, 6-diene (3, R=SO$_2$Ph) with LAH was conducted at room temperature. Under these conditions a good yield of 2-azabicyclo[3.2.1]oct-6-ene (6, R=H) was obtained and this could be converted to the sulphonamide (6, R=SO$_2$Ph), C$_{13}$H$_{15}$NO$_2$S, on treatment with phenylsulphonyl chloride and base. The structure was confirmed by extensive decoupling experiments† and catalytic reduction gave N-phenylsulphonyl-2-azabicyclo[3.2.1]octane (7, R=SO$_2$Ph) identical in all respects with an authentic sample.[6] The final member of the phenylsulphonamide series, N-phenylsulphonyl-2-azabicyclo[3.2.1]oct-3-ene (8, R=SO$_2$Ph) was prepared by selective reduction of the less electron-rich olefin in the diene (3, R=SO$_2$Ph) by diimide. Reduction of the 3-ene (8, R=SO$_2$Ph) with LiAlH$_4$ yielded the amine (7, R=H) which could be converted to the sulphonamide (7, R=SO$_2$Ph) identical in all respects to an authentic sample.[6] We had now prepared the diene (3, R=SO$_2$Ph) and all of its possible reduction products. ^{1}H NMR spectra were especially rich in detail and decoupling experiments† allowed assignment of chemical shifts with certainty, an important point in our subsequent analysis of possible homoconjugative effects.[1]

N-Carbomethoxy-2-azabicyclo[3.2.1]octa-3, 6-diene (3, R=CO$_2$Me)[7] was prepared from the known[8] nitrile (3, R=CN) on treatment with methanolic base, or by heating the known[10] tricyclic urethane (9) in methanol to obtain the diene (3, R=CO$_2$Et) followed by transesterification. The ^{1}H NMR spectral chemical shift assignments were in

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†^{1}H NMR spectra and decoupling experiments are described in full in the experimental section.

line with values for the sulphonamide (3, R=SO$_2$Ph).† Selective reduction of the less electron-rich olefin in the diene (3, R=CO$_2$Me) readily gave the 3-ene (**8**, R=CO$_2$Me). The ^{1}H NMR spectrum of this compound was very rich in detail† and it was evident that geometrical isomerism due to restricted rotation of the urethane C–N bond was a complicating feature. This was removed in the spectrum at +60° and extensive decoupling experiments† allowed a full analysis of the spectrum. N - Carbomethoxy - 2 - azabicyclo[3.2.1]oct - 6 - ene (**6**, R=CO$_2$Me) was obtained by reaction of the amine (**6**, R=H) with methyl chloroformate and the fully saturated N - carbomethoxy - 2 - azabicyclo - [3.2.1]octane (7, R=CO$_2$Me) was obtained from either the diene (3, R=CO$_2$Me) or the 3-ene (**8**, R=CO$_2$Me) by catalytic reduction.

Having prepared two complete series of aza-compounds with electron-withdrawing groups on nitrogen, it was of interest to prepare either the parent series (3, **6**, 7 and **8**, R=H), or N-alkylated derivatives of this parent series, since the resultant dienes (3) would be expected to be much more likely to show conjugative effects involving the lone-pair if the electron withdrawing group were not present. In the parent series we had already prepared the 6-ene (**6**, R=H) by LAH reduction of the sulphonamide (3, R=SO$_2$Ph). The "3-ene" (**8**, R=H) had been postulated[11] as an intermediate in the reductive amination of 2-*exo*-chloronorbornane (**10**) although it was felt to exist as the imine (11). To verify this unproven postulate[11] we synthesed the imine (11) from the known[12] aldehyde (12, X=O, R=H) by conversion to the ketal (12, X=OCH$_2$CH$_2$O, R=H), reduction to the dihydroderivative (13) and removal of the protecting groups with concomitant cyclisation. The product was, as expected, fairly unstable but the spectral characteristics were in keeping with its formulation as the imine (11). Further, reduction with sodium borohydride gave the amine, (7, R=H) which could be converted to the sulphonamide (7, R=SO$_2$Ph), identical in all respects with an authentic sample.[6]

Since the imine (11) had been formed rather than the enamine (**8**, R=H), it was of interest to prepare the diene (3, R=H) to see whether in fact the presence of the 6-ene would cause this compound to exist as the 3, 6-diene or whether it would take the form of the alternative 2, 6-diene. The diene (3, R=H) was made by addition of ammonia to a solution of the aldehyde ((2, X=O)$\rightleftharpoons$(1)) at low temperatures. The product was unstable and it was therefore not possible to obtain a completely pure sample. Although dimerisation occurred within 15 min at room temperature, use of low temperature techniques allowed spectra to be recorded. Quartets characteristic of H$_6$ and H$_7$ in the dienes (3) were present in the ^{1}H NMR spectrum but there was no absorption characteristic of the enamine proton H$_3$ which occurred between τ 4.22 and τ4.58 in the spectra of the dienes (3, R = alkyl).[1] Instead a doublet with chemical shift more in keeping with the imine proton H$_3$ in 2-azabicyclo[3.2.1]octa-2, 6-diene was present. The compound could be converted to the sulphonamide (3, R=SO$_2$Ph) in small yield. The occurrence of the imine form is in keeping with the findings of Anastassiou[9,13] and might be held to argue against any excessive homoconjugative stabilisation in the dienes (3).

The reaction of the aldehyde [2(X=O)$\rightleftharpoons$1] with ammonia and amines seemed potentially useful for synthesis of the N-alkylated dienes (3). We had previously shown[12] that reaction of the aldehyde [2 (X=O)$\rightleftharpoons$1] with excess of methylamine had led to the valence isomers (14$\rightleftharpoons$15), but, when one or two equivalents of methylamine were used, a product with the characteristic ^{1}H NMR spectrum of the diene (3, R=Me) was obtained. This compound was very unstable and dimerised readily at room temperature so that low temperature techniques were employed to obtain spectra. The diene (3, R=Me) was also prepared by two alternative routes, either by reduction of the urethane (3, R=CO$_2$Me) with LAH or by methylation of the ketal (12, X=OCH$_2$CH$_2$O, R=H) to (12, X=OCH$_2$CH$_2$O, R=Me) followed by deprotection and concomitant cyclisation. Catalytic reduction of the diene (3, R=Me) gave N-methyl-2-azabicyclo[3.2.1]octane (7, R=Me) spectrally identical with an authentic sample.[6] N-Methyl-2-azabicyclo[3.2.1]oct-6-ene (**6**, R=Me) was prepared by methylation of the "parent" compound (**6**, R=H) or by reduction of the urethane (**6**, R=CO$_2$Me) with LAH. The 6-ene (**6**, R=Me) was more stable than the diene (3, R=Me) but it was still found advisable to use low temperature techniques for its isolation. Reduction of the urethane (**8**, R=CO$_2$Me) with LAH afforded the final compound of the N-methyl series, N-methyl-2-azabicyclo[3.2.1]oct-3-ene(**8**, R=Me). This was again unstable and dimerised at room temperature so that low temperature techniques were employed in its isolation and handling.

The N-ethyl and N-t-butyl dienes (3, R = Et and R = Bu^t) were prepared by reaction of the aldehyde [2, (X = O) $\rightleftharpoons$ 1] with the appropriate amine, and it was observed that the stability of the compounds in the series (3, R = alkyl) increased with increasing size of the alkyl substituent. It was further evident from the ^{1}H NMR spectra (see for example Fig. 1) that the dienes (3, R = alkyl) coexisted with their Cope rearrangement products, the imines (2, X=NR), at room temperature. We had noted that the equilibrium [2(X = O) $\rightleftharpoons$ 1] could be shifted towards the diene (1) by use of NMR spectral solvents of relatively low dielectric constant such as carbon tetrachloride and use of this solvent was very effective in shifting the equilibrium in the aza-series towards the diene (3). The observation of the ready equilibrium (2, X=NR)$\rightleftharpoons$(3, R = alkyl) in the alkyl series where we had expected bishomoconjugative stabilisation of the diene (3) to be more apparent than in the dienes (3, R=SO$_2$Ph or CO$_2$Me), where the diene form was the only isomer observed at room temperature, might be taken as arguing against homoconjugative stabilisation effects operating in the dienes (3).

The fully saturated N-t-butyl-2-azabicyclo[3.2.1]octane (7, R=Bu^t) was prepared from the diene (3, R=Bu^t) by catalytic reduction and separation of the desired product from a product of reduction of the imine form (2, X=NBu^t) by preparative glc.

Since reaction of the aldehyde [2 (X=O)$\rightleftharpoons$1] with amines had proved to be such an effective method of preparing dienes in the aza-series, an attempt was made to prepare 2-thiabicyclo[3.2.1]octa-3,6-diene (**16**) by reaction of the aldehyde [2 (X=O)$\rightleftharpoons$1] with H$_2$S and HCl. The product of this reaction had spectral data† in accord with the hemithioacetal structure (17, R=H) and it could be acetylated to a thioacetate (17, R=COMe). The reaction proved concentration-dependent, since at higher concentrations of aldehyde a compound with data

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†^{1}H NMR spectra and decoupling experiments are described in full in the experimental section.

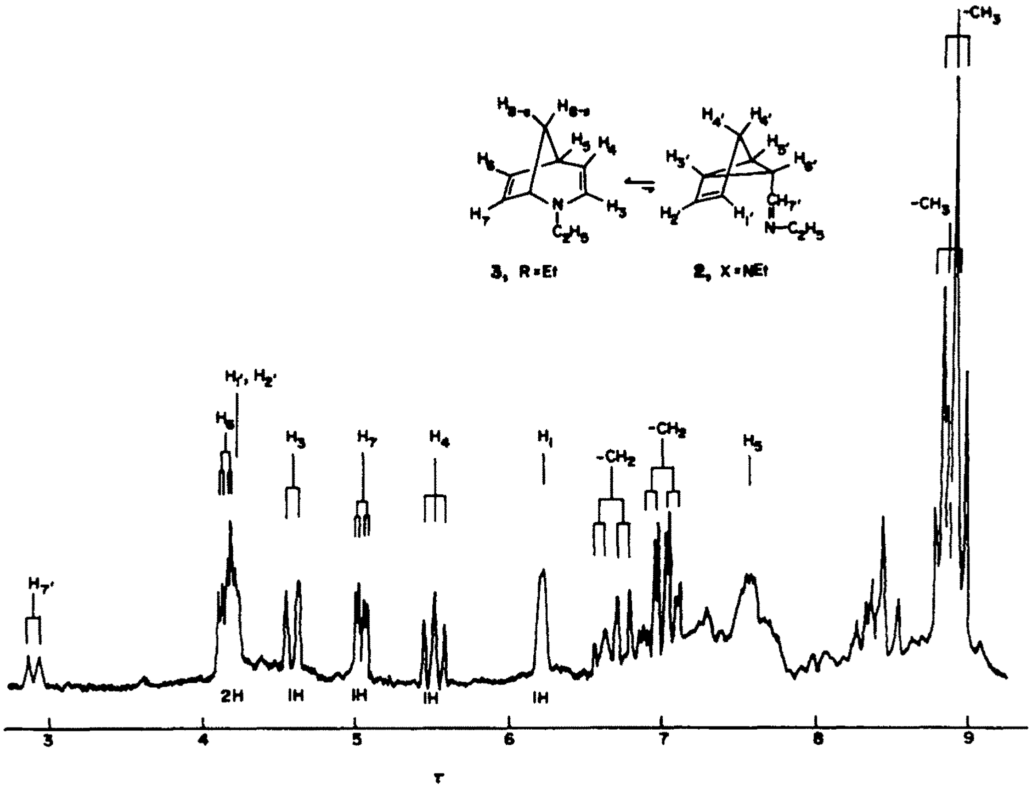
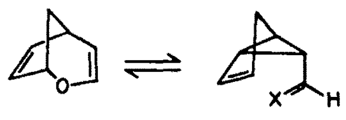


Fig. 1. ¹H NMR spectrum of the diene (3, R=Et) in CCl₄



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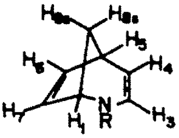

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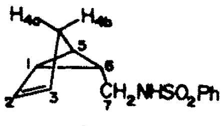

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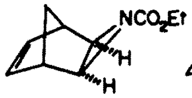

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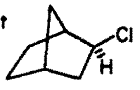

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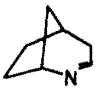

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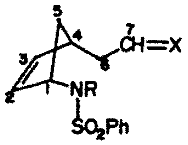

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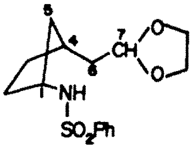

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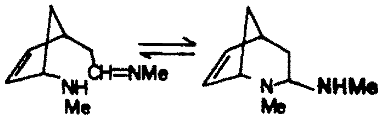

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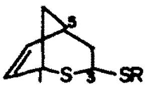

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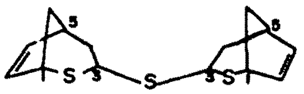

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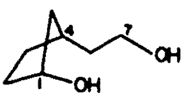

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consistent with the structure 18 was obtained. At this stage in our work, Fujisawa[14] reported synthesis of 2-thiabicyclo[3.2.1]octa-3, 6-diene (16) and we were able to use his method[15] to prepare this diene and the corresponding sulphone and sulphoxide. 2-Thiabicyclo[3.2.1]oct-3-ene (19) was prepared from the diene (16) by selective reduction of the Δ^6-olefinic bond with di-imide, and the fully saturated 2-thiabicyclo[3.2.1]octane (20) was obtained from the known[3] diol (21) in low yield by conversion to the dibromide and reaction with sodium sulphide. This latter compound was identical with an authentic sample obtained from Iranian kerosine oil.[16]

We have now prepared a large variety of 2-heterobicyclo[3.2.1]octa-3, 6-dienes and their reduced derivatives with a view to studying possible bishomoconjugative effects in this system. *Data showing* that the equilibrium between the 3, 6-diene (3, R=H) and the isomeric 2, 6-diene favours the latter isomer, and that the equilibrium $3 \rightleftharpoons 2$ in the aza series has more of the imine form 2 as the substituent on nitrogen becomes less electron-withdrawing would *not* seem to suggest that there is any special bishomoconjugative stabilisation in the nitrogen series (3).

EXPERIMENTAL

M.ps. were determined with a Kofler hot stage apparatus. IR spectra were recorded using a Perkin Elmer 237 instrument. NMR spectra were recorded at Sussex using Varian HA100 or Perkin Elmer R32 instruments and at P.C.M.U., Harwell using Varian and Perkin Elmer 220 MHz machines. Mass spectra were obtained using Hitachi RMU6, A.E.I.M.S.9, or A.E.I.M.S. 30 instruments by Mr. A. Greenway. Glc was performed by Mr. C. Simpson and his staff using Pye-Unicam 104/64 instruments with a flow rate of 50 ml min^{-1} N_2. Tlc was performed using Merck Kieselgel GF254 in 0.25 mm layers for analytical work and 0.75 mm layers for preparative work. We thank Mr. and Mrs. A. G. Olney for microanalyses.

N - *Phenylsulphonyl* - 2 - *azabicyclo*[3.2.1]*octa* - 3, 6 - *diene* (3, $R=SO_2Ph$) was prepared by the method of Oehlschlager and Zalkow[4] but ^1H NMR-spectral assignments[4] were revised in the light of decoupling experiments, τ ($CDCl_3$) 2.1–2.6 (5H, m, aromatics), 3.74 (1H, dxd, $J_{3,4}$ 7.5 Hz, $J_{1,3}$ 1.5 Hz, H_3 which on irradiation of H_1, τ 5.27, collapsed to d, J 7.5 Hz), 3.94 (1H, dxd, $J_{6,7}$ 6 Hz, $J_{5,6}$ 2.5 Hz, H_6 which on irradiation at H_5, τ 7.36, collapsed to d, J 6Hz), 4.76 (1H, t, J 7.5 Hz, H_4) 4.82 (1H, dxd, $J_{6,7}$ 6Hz, $J_{1,7}$ 3Hz, H_7 which on irradiation at H_1, τ 5.27, collapsed to d, J 6Hz), 5.27 (1H, brs, H_1), 7.36 (1H, m, H_5), 8.28 (1H, m, H_{8a} which simplified somewhat on irradiation at H_5, τ7.36), 8.68 (1H, d, $J_{8a,8s}$ 10 Hz, H_{8s}).

Reduction of N-*phenylsulphonyl*-2-*azabicyclo*[3.2.1]*octa*-3, 6-*diene* (3, $R=SO_2Ph$) *with* LAH *in refluxing tetrahydrofuran*. A soln of 3, ($R=SO_2Ph$; 1.5 g) in dry THF (25 ml) was added to a stirred suspension of LAH (400 mg) in dry THF (25 ml) over a period of 20 min. The mixture was heated at reflux for 14 hr, cooled, and the excess LAH was destroyed by careful addition of MeOH and then water. The mixture was filtered and the filtrate was concentrated *in vacuo*, diluted with water and extracted with $CHCl_3$. The extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo* to yield a yellow oil (1.15 g) which was purified by preparative tlc (SiO_2, $CHCl_3$) to yield 4 as a semi-solid (659 mg, 44%) which was pure by glc on 5 ft 5% SE30 at 190°, (Found; *m/e* 249.08184; $C_{13}H_{15}NO_2S$ requires: 249.08234); $\nu_{max}^{CHCl_3}$ 3295 cm^{-1} (NH); τ ($CDCl_3$) 2.22 and 2.58 (5H, m, aromatics), 4.67 (2H, m, olefinics), 5.28 (1H, brt, J5Hz, NH, exchangeable in D_2O), 7.20 and 7.47 (2H, octet, $J_{7,7'}$ 12Hz, $J_{7,6}$ 7Hz, $7_{7',6}$ 8Hz, H_7), 7.58 (1H, dxd, J 18Hz and 7Hz, H_4), 8.18 (2H, m + d, $H_{6'}+H_1$), 8.46 (1H, q, H_3), 8.96 (1H, sextet, H_6).

(7RS) [7-$^2H_1$) - N - *Phenylsulphonyl* - endo - 6 - *aminomethylbicyclo*[3.1.0]*hex-2-ene* was prepared as above but with LAD substituted for LAH. The product, *m/e* 250, had an identical ^1H NMR spectrum to the undeuterated sample except that the τ 7.20 and 7.47 absorptions were doublets (J=7 Hz and 8 Hz respectively) and the absorption at τ 8.96 was a quartet.

endo-6-*Carbamoylbicyclo*[3.1.0]*hex-2-ene* (5, $R=NH_2$) The acid[5] 5, (R=OH; 1.0 g) was treated dropwise with redist. $SOCl_2$ (5 ml) over 5 min and left for 1.5 hr at room temp. Excess $SOCl_2$ was removed *in vacuo* leaving (5, R=Cl) as an oil, ν_{max}^{film} 1783 cm^{-1} (COCl). This was dissolved immediately in dry ether (20 ml) and the soln was added slowly to an ethereal soln (20 ml) through which a continuous stream of ammonia was passed. Ammonia was passed for 1 hr after completion of the addition and the mixture was filtered and the ppt washed with dry ether. The combined ethereal solns were concentrated *in vacuo* to yield a solid which was purified by sublimation at 72° and 0.5 mm Hg, m.p. 112–114°, (Found: *m/e* 123.06881, C_7H_9NO requires: 123.06841), $\nu_{max}^{CHCl_3}$ 3380 (NH) and 1665 cm^{-1} (amide), τ($CDCl_3$) 4.30 (2H, m, olefinic), 7.28–8.40 (5H, complex).

N-*Phenylsulphonyl*-endo-6-*aminomethylbicyclo*[3.1.0]*hex-2-ene*(4). The amide 5, ($R=NH_2$; 360 mg) was dissolved in dry ether (4 ml) and added dropwise to a stirred suspension of LAH (350 mg) in dry ether (20 ml) over 15 min, and stirring was continued for 14 hr at room temp. Excess LAH was destroyed by careful addition of MeOH and then water and the mixture was filtered. The filtrate was concentrated *in vacuo*, diluted with water and extracted with $CHCl_3$. The extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo* to yield the amine as a yellow oil which decomposed on attempted purification. The crude amine (100 mg) was dissolved in anhyd pyridine (3 ml) with phenylsulphonyl chloride (200 mg). The soln was left at room temp for 5 hr, poured onto 2N HCl (10 ml) and extracted with $CHCl_3$. The extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo* to yield a brown oil which was purified by preparative tlc (SiO_2; $CHCl_3$) to yield a pure semi-solid (100 mg, 44%) with identical IR, ^1H NMR and mass spectra to the sample of 4 obtained by reduction of 3, ($R=SO_2Ph$) with LAH in refluxing THF.

2-*Azabicyclo*[3.2.1]*oct-6-ene*(6, R=H). The sulphonamide 3, ($R=SO_2Ph$; 1.0 g in 20 ml dry THF) was added dropwise over 40 min to a stirred suspension of LAH (600 mg) in dry THF (50 ml) and stirring was continued for 14 hr at room temp. Excess LAH was destroyed by careful addition of water and the mixture was filtered and the filtrate extracted with $CHCl_3$. The extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo* to yield a yellow oil (316 mg, 72%). The product was purified first by distillation at 20° and 0.12 mm Hg and then by preparative glc on 5 ft 5% apiezon–4% KOH at 100° to yield a liquid (Found: *m/e* 109.088615, $C_7H_{11}N$ requires: 109.089145); $\nu_{max}^{CHCl_3}$ 3290 cm^{-1} (NH); τ ($CDCl_3$) 3.89 (1H, dxd, J 6Hz and 3Hz, H_6) 4.22 (1H, dxd, J 6Hz and 3Hz, H_7), 6.28 (1H, brs, NH, exchangeable in D_2O), 6.35 (1 H, brs, H_1), 6.90 (1 H, dxd, J12Hz and 6Hz, *endo* H_3), 7.22 (1H, txd, J 12Hz and 5Hz, *exo* H_3), 7.40 (1H, brs, H_5), 8.12 (1H, dxd, J 10Hz and 3Hz, H_{8a}), 8.29 (1H, dxd, J 12Hz and 6Hz, *exo* H_4), 8.44 (1H, d, J 10Hz, H_{8s}), 8.69 (1H, br, *endo* H_4).

N-*Phenylsulphonyl*-2-*azabicyclo*[3.2.1]*oct-6-ene* (6, $R=SO_2Ph$), Phenylsulphonyl chloride (128 mg) was added to a soln of 6, R=H; 89 mg) in 2N NaOH (6 ml) and the soln was stirred at room temp. for 1 hr. The mixture was extracted with $CHCl_3$ and extracts were dried (Na_2SO_4). The solvent was removed *in vacuo* to yield a semi-solid (144 mg, 57%) which on preparative tlc (SiO_2; $CHCl_3$) gave a solid (64 mg, 22%) m.p. 93–94.5°. Further purifiication was effected by sublimation at 135° and 7 mm Hg (Found: C, 63.4; H, 6.1; N, 5.6%, $C_{13}H_{15}NO_2S$ requires: C, 62.6; H, 6.0; N, 5.6%), *m/e* 249 (M^+), τ ($CDCl_3$) 2.2–2.49 (5H, m, aromatics), 4.0 (1H, dxd, J 6Hz, and 3Hz, H_6, which collapsed to d, J, 6Hz, on irradiation at H_5, τ 7.39 and to d, J 3Hz, on irradiation at H_7, τ 4.85), 4.85 (1H, dxd, J 6Hz and 3Hz, H_7 which collapsed to d, J 6Hz, on irradiation at H_1, τ 5.36, and to d, J 3Hz, on irradiation at H_6, τ 4.0), 5.36 (1H, m, H_1), 6.41 (1H, dxd, J 12Hz and 6Hz, *endo* H_3, which collapsed to d, J 12Hz, on irradiation at *exo* H_4, τ 8.24), 7.28 (1H, txd, J 12Hz and 5Hz, *exo* H_3, which collapsed to t, J 12Hz, on irradiation at *endo* H_4, τ 8.64), 7.39 (1H, brs, H_5), 8.10 (1H, m, H_{8a}, which collapsed to brd, J 12 Hz, on irradiation at H_5, τ 7.39), 8.24 (1H, dxd, J 12 Hz and 6Hz, *exo* H_4, which collapsed to d, J 12Hz, on irradiation of *endo*

H_3 at τ 6.41), 8.39 (1H, d, J 12Hz, H_{8s}), 8.64 (1H, brd, *endo* H_4, which collapsed to d, J 12Hz, on irradiation at H_5, τ 7.39).

N-*Phenylsulphonyl-2-azabicyclo*[3.2.1]*octane* (7, R=SO_2Ph). 10% Pd-C (32 mg) was suspended in a soln of 6, R=SO_2Ph) (57 mg) in MeOH (25 ml) and the mixture was stirred under H_2 at room temp. and pressure until uptake had ceased (45 min). The soln was filtered and the solvent was removed *in vacuo* to yield a solid (45 mg, 80%), m.p. 74–76° (lit[6]. 74–76°), which had identical spectra to an authentic sample of 7, (R=SO_2Ph).

N-*Phenylsulphonyl-2-azabicyclo*[3.2.1]*oct-3-ene* (8, R=SO_2Ph) was prepared either by selective catalytic reduction of 3, (R=SO_2Ph)[4] or by reduction of this diene (92 mg) in MeOH (15 ml) using potassium azodicarboxylate (92 mg) with addition of AcOH (29 mg) in MeOH (10 ml) over 15 min at room temp. The product had the expected properties.[4]

2-*Azabicyclo*[3.2.1]*octane* (7, R=H). The sulphonamide 8, (R = SO_2Ph; 320 mg) was dissolved in dry ether (15 ml) and added over 30 min to a stirred suspension of LAH (230 mg) in dry ether (25 ml) under N_2. The mixture was stirred at room temp. for 22 hr and excess LAH was destroyed by careful addition of 1 N NaOH (1 ml). The soln was filtered, separated and dried (Na_2SO_4). The solvent was removed *in vacuo* at 30° to yield a product (21 mg) with the expected[6] spectra. This could be converted directly to 7 (R=SO_2Ph; 25 mg) as in the preparation of 6, (R=SO_2Ph) above. The product was identical in all respects to an authentic sample of 7, (R=SO_2Ph).[6]

N-*Carbethoxy-2-azabicyclo*[3.2.1]*octa-3,6-diene* (3, R=CO_2Et). A soln of 9[10] (40 g) in MeOH (220 ml) was heated to 60° for 12 hr. The solvent was removed *in vacuo* and the residue was distilled to yield a fraction, bp 58–60° at 0.5 mm Hg, as an oil (30 g, 75%), (Found: C, 66.8; H, 7.1; N, 7.95. $C_{10}H_{13}NO_2$ requires: C, 67.0; H, 7.3; N, 7.8%). *m/e* 179 (M^+), ν_{max}^{film} 1710, 1660, 1620 cm^{-1}; τ ($CDCl_3$) 3.64 (1H, brd, J 8Hz, H_3), 3.85 (1H, dxd, J 6Hz and 3Hz, H_6), 4.54 (1H, dxd, J 6Hz and 3Hz, H_7), 4.86 (1H, t, J 7Hz, H_4), 4.97 (1H, m, H_1), 5.82 (2H, q, J 7Hz, CH_2CH_3. 7.28 (1H, m, H_5), 8.28 (2H, m, H_8), 8.72 (3H, t, J 7Hz, CH_2CH_3).

N - *Carbomethoxy* - 2 - *azabicyclo*[3.2.1]*octa* - 3,6 - *diene* (3, R = CO_2Me).

Method A. A soln of 3, (R=CO_2Et; 15 g) in MeOH (80 ml) containing NaOH (1g) was heated at reflux for 2 hr. The soln was concentrated *in vacuo*, diluted with water and extracted with $CHCl_3$. The extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo*. The residue distilled at 62–64° and 0.6 mm Hg to yield a colourless oil, (10.1 g, 73%), (Found: C, 65.0; H, 6.95; N, 8.65%. $C_9H_{11}NO_2$ requires: C, 65.45; H, 6.7; N, 8.5%), *m/e* 165 (M^+), ν_{max}^{film} 1715, 1660, 1625 cm^{-1}, τ ($CDCl_3$) 3.66 (1H, brd, J 8Hz, H_3), 3.81 (1H, dxd, J 6Hz and 2.5Hz, H_6), 4.52 (1H, dxd, J 6Hz, and 2.5Hz, H_7), 4.83 (1H, t, J 8Hz, H_4), 4.96 (1H, m, H_1) 6.27 (3H, s, CO_2Me), 7.28 (1*H*, *m*, H_5), 8.20 (2*H*, *m*, H_8).

Method B. Heating a soln of 3, (R=CN[6]: 200 mg) in MeOH (10 ml) containing KOH (350 mg) at reflux for 60 hr gave on work-up a 40% yield of the above 3, (R=CO_2Me).

N-*Carbomethoxy-2-azabicyclo*[3.2.1]*oct-3-ene* (8, R=CO_2Me). Potassium azodicarboxylate (535 mg) was added to an ice-cooled soln of 3, (R=CO_2Me; 460 mg) in MeOH (50 ml) under N_2. AcOH (167 mg in 10 ml MeOH) was added to the soln over 20 min and the mixture was stirred at 0° for a further 40 min. The solvent was removed *in vacuo* and the residue was extracted with $CHCl_3$. The extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo* to give a product (396 mg, 74%) which was distilled at 43° and 5 mm Hg as a liquid, pure by glc on 9ft 5% carbowax—2% KOH at 150°, (Found: C, 64.25; H, 8.0; N, 8.4 $C_9H_{13}NO_2$ requires: C, 64.6; H, 7.8; N, 8.4%); *m/e* 167 (M^+), $\nu_{max}^{CHCl_3}$ 1685 cm^{-1} (NCO_2Me), τ ($CDCl_3$) 3.39 and 3.52 (1H, 2xd, J 7Hz, H_3 in isomers), 4.80 and 4.90 (1H, 2xt, J 7Hz, H_4 in isomers, collapsing to 2xd, J 7Hz or irradiation at H_5, τ 7.6), 5.22 and 5.38 (1H, 2x brs, H, which sharpened on irradiation at *exo* H_7, τ 8.0). The remainder of the ^1H NMR spectrum was unaffected by the geometrical isomerism and was identical to the upper part of the higher temp. spectrum, τ ($CDCl_3$, +60°C) 3.48 (1H, J 7Hz, H_3) 4.88 (1H, t, J 7Hz, H_4), 5.28 (1H, m, H_1), 6.28 (3H, s, CO_2Me), 7.60 (1H, m, H_5), 8.0 (1 h, dxd, J 7Hz and 12Hz, *endo* H_7, which collapsed to d, J 12Hz on irradiation at H_1, τ 5.28), 8.06–8.14 (2H, m, *exo* H_6 + *exo* H_7), 8.20 (1H, d, J 12Hz, H_{8s}), 8.27 (1H, t, *endo* H_6), 8.38 (1H, m, H_{8a}, which collapsed to dJ 12Hz on irradiation at H_1, τ 5.28).

N-*Carbomethoxy-2-azabicyclo*[3.2.1]*oct-6-ene* (6, R=CO_2Me), A soln of NaOH (1.72g in 25 ml water) was added to a soln of 6, (R=H; 194 mg) in $CHCl_3$ (50 ml) with stirring. The soln was cooled in an ice-bath and methyl chloroformate (282 mg) was added over 15 min. Stirring was continued for 1 hr at 0° and the soln was acidified with 6 N HCl and stirred for a further 30 min at room temp. The mixture was extracted with $CHCl_3$ and the combined extracts were dried (Na_2SO_4). The solvent was removed *in vacuo* at room temp. to yield a yellow oil which purified on preparative tlc (SiO_2: 9 $CHCl_3$, 1 MeOH) as a liquid, (138 mg, 90%) which distilled at 80–82° and 13 mm Hg, pure by glc, (Found: C, 64.5; H, 7.9; N, 8.4: $C_9H_{13}NO_2$ requires; C, 64.6; H, 7.8; N, 8.4%), *m/e* 167 (M^+) $\nu_{max}^{CHCl_3}$ 1690 cm^{-1} (NCO_2Me) τ ($CDCl_3$) 3.79 (1H, dxd, J 6Hz and 3Hz, H_6 which collapsed to d, J 6Hz, on irradiation at H_5, τ 7.30), 4.12 (1H, dxd, J 6Hz and 3Hz, H_7, which collapsed to d, J 6Hz, on irradiation at H_1, τ 5.08), 5.08 (1H, brs, H_1), 6.18 (1H, br, *endo* H_3), 6.32 (3H, s, CO_2Me), 6.93 (1H, txd J 12Hz and 6Hz, *exo* H_3, which collapsed to t, J 12Hz, on irradiation at *endo* H_4, τ 8.56), 7.30 (1H, m, H_5), 8.09 (1H, m, H_{8a} sharpens on irradiation at H_5, τ 7.30), 8.25 (1H, m, *exo* H_4), 8.47 (1H, d, J 11Hz, H_{8s}), 8.56 (1H, m, *endo* H_4).

N-*Carbomethoxy-2-azabicyclo*[3.2.1]*octane* (7, R=CO_2Me). 10% Pd-C (684 mg) was added to a soln of 3, (R=CO_2Me; 1.5 g) in MeOH (100 ml) and the mixture was stirred under H_2 at room temp. and pressure for 2 days. The soln was filtered and the solvent was removed *in vacuo* to yield a liquid which distilled at 93–95° and 1.75 mm Hg (1.13 g 75%), pure by glc, (Found: C, 63.6; H, 8.9; N, 8.5: $C_9H_{15}NO_2$ requires: C, 63.9; H, 8.9; N, 8.3%), *m/e* 169 (M^+), $\nu_{max}^{CHCl_3}$ 1674 cm^{-1} (NCO_2Me), τ ($CDCl_3$) 5.43 (1H, brs, H_1), 6.13 (1H, br, *endo* H_3), 6.36 (3H, s, CO_2Me), 7.01 (1H, dxt, J 12Hz and 6Hz, *exo* H_3), 7.36 (1H, brs, H_5), 8.33–8.50 (8H, complex). Reduction of 8, (R=CO_2Me) for 3 hr by this method also yielded the above product.

2-(4-*Phenylsulphonylaminocyclopent-2-enyl*)*acetaldehyde ethylene ketal* (12, X=OCH_2CH_2O, R=H). The aldehyde 12, (X=O, R=H; 12 g) was suspended in ethane-1,2-diol (13 ml) with triethyl orthoformate (24 ml) and the mixture was heated at 60° until homogeneous, when *para*-toluenesulphonic acid (200 mg) was added. The soln was heated to 100° for 1.5 hr and cooled. NaOH (1g) was added and the mixture was shaken with $CHCl_3$. The organic soln was washed well with water and dried (Na_2SO_4). Removal of the solvent *in vacuo* gave an oil which was chromatographed (SiO_2). Elution with ether gave a semi-solid (9.8 g, 70%) which was further purified by preparative tlc (SiO_2, $CHCl_3$), *m/e* 309 (M^+), $\nu_{max}^{CHCl_3}$, 3340 cm^{-1} (NH), τ ($CDCl_3$) 2.10 and 2.44 (5H, m, aromatics), 4.18 (1H, dxt, J 6Hz and 2Hz, olefinic), 4.54 (1H, dxt, J 6Hz and 2Hz, olefinic), 4.73 (1H, d, J 9Hz, NH, exchangeable in D_2O), 5.18 (1H, t, J 6Hz, H_7), 5.64 (1H, m, H_1), 6.12 (4H, A_2B_2, CH_2O), 7.31 (1H, m, H_4), 7.62 (1H, dxt, J 14Hz and 7Hz, H_5), 8.30 (2H, t, J 7Hz, H_6), 8.76 (1H, pent, $H_{5'}$).

2-(3-*Phenylsulphonylaminocyclopentyl*)*acetaldehyde ethylene ketal* (13). The ketal 12, (X=OCH_2CH_2O, R=H; 4 g) and 10% Pd-C (250 mg) in MeOH (60 ml) were shaken in H_2 at room temp. and pressure until uptake of gas had ceased (*ca.* 4 hr). The soln was filtered and the filtrate concentrated *in vacuo* and chromatographed (SiO_2). Elution with benzene: ether (3:2) gave an oil (3.1 g, 77%) which was further purified by preparative tlc (SiO_2; 95$CHCl_3$: 5MeOH), *m/e* 311 (M^+), $\nu_{max}^{CHCl_3}$ 3345, 3250 cm^{-1} (NH), τ ($CDCl_3$) 2.10 and 2.5 (5H, m aromatics), 5.24 (1H, t, J 6Hz, H_7), 6.16 (4H, A_2B_2, CH_2O), 6.40 (1H, m, H_1), 7.54–9.0 (9H, m).

2-*Azabicyclo*[3.2.1]*oct-2-ene* (11), Na (2.5 g) was added in small pieces to a soln of 13 (2.0 g) in *sec*-BuOH (25 ml) over 15 min at room temp. and the reaction was heated to reflux overnight. The soln was cooled, diluted with water and acidified with 5N HCl. The mixture was concentrated *in vacuo* and extracted with $CHCl_3$. The aqueous layer was make alkaline with KOH aq and extracted with $CHCl_3$. These latter extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo* to yield a yellow oil (350 mg) which solidified on cooling. A sample distilling at room temp. and low pressure was pure by tlc. It decomposed at room temp. but could be stored at −78°, *m/e* 109, $\nu_{max}^{CHCl_3}$ 1663 cm^{-1} (C=N), τ ($CDCl_3$) 2.48 (1H, brs, H_3), 5.88 (1H, brs, H_1), 7.4–8.8 (9H, m). The cruder sample of imine (150 mg) was reduced with $NaBH_4$ (100 mg) in MeOH (6 ml) at room temp. overnight and worked up to give the crude 7, (R=H) which was directly treated with phenylsulphonyl chloride and NaOH aq as described in the preparation of 6, (R = SO_2Ph) above. The crude product was purified by preparative tlc (SiO_2; $CHCl_3$) and had identical spectra to an authentic sample of 7, (R=SO_2Ph).[6] A m.m.p. was undepressed.

2-*Azabicyclo*[3.2.1]*octa*-2, 6-*diene*. Gaseous ammonia was passed through a suspension of [2, (X=O)$\rightleftharpoons$1] (1g) and anhyd $MgSO_4$ (1.5g) in dry benzene (50 ml) for 3 hr at ambient temp. with stirring. The mixture was filtered and the solvent was removed *in vacuo* at low temp. to give a product which, although unstable, could be stored in dilute solution in $CHCl_3$ at −78°, ν_{max}^{film} 1660 cm^{-1}, *m/e* 107 (M^+), τ ($CDCl_3$, −30°C) 2.80 (d, J 8Hz, H_3), 3.68 (dxd, J 6Hz and 2.75 Hz, H_6), 3.95 (dxd, J6 and 2.75 Hz, H_7), 4.24 (m), 5.66 (m), etc. Treatment with phenylsulphonyl chloride and base as above gave a small yield of 3, R=SO_2Ph).

N-*Methyl-2-azabicyclo*[3.2.1]*octa*-3, 6-*diene* (3, R=Me)

Method A. A soln of methylamine (400 mg) in dry benzene (2 ml) was added over 15 min to a suspension of [2, (X=O)$\rightleftharpoons$1] (200 mg) in dry benzene (3 ml) at room temp. The mixture was stirred for a further 15 min and filtered. The solvent was removed *in vacuo* at room temp. to yield 3, (R=Me) as an unstable oil, (135 mg), *m/e* 121 (M^+), τ($CDCl_3$) 3.88 (dxd, J6Hz and 3Hz, H_6), 4.46 (d, J 8Hz, H_3). 4.80 (dxd, J 6Hz and 2.75Hz, H_7), 5.20 (t, J 8Hz, H_4), 6.22 (brs, H_1), 7.52 (s, NMe) and other absorptions.

Method B. A soln of 3, (R=CO_2Me; 214 mg) in dry ether (10 ml) was added to a stirred suspension of LAH in dry ether (15 ml) under N_2 and stirring was continued at room temp. overnight. Excess LAH was destroyed by careful addition of 2N. NaOH and the mixture was filtered and extracted with ether. The combined ethereal layers were dried (Na_2SO_4) and the solvent was removed *in vacuo* to yield an oil (143 mg) with the characteristic ^1H NMR spectrum of 3, (R=Me) above. Dimerisation to an oil *m/e* 242, occurred rapidly at room temp.

Method C. MeI (12 ml) was added to a soln of 12, (X=OCH_2CH_2O, R=H; 1.5 g) in 1:1 aqueous MeOH (30 ml) containing NaOH (1.0 g) and the reaction was stirred at room temp. for 24 hr and extracted with CH_2Cl_2. The extracts were washed with dil HCl and brine and dried (Na_2SO_4). Removal of the solvent *in vacuo* gave an oil which was chromatographed (SiO_2). Elution with benzene: ether (1:3) gave 12, (X=OCH_2CH_2O, R=Me; 860 mg) which was further purified by preparative tlc (SiO_2:$CHCl_3$) *m/e* 182 ($M^+ - SO_2Ph$), τ ($CDCl_3$) 2.14 and 2.44 (5H, m, aromatics), 4.14 and 4.71 (2H, 2Xm, olefinics), 4.86 (1H, brt, H_1), 5.04 and 5.53 (1H, 2xt, J 6Hz, H_7), 6.12·(4H, m, OCH_2), 7.35 (3H, s, NMe), 7.72 (2H, m, $H_4 + H_5$), 8.30 (2H, m, H_6), 8.84 (1H, pent, H_5). The ketal was treated with sodium and *sec*-butanol with an acidic work-up exactly as in the preparation of 11 above to yield 3 with ^1H NMR spectral absorptions as above.

Catalytic reduction of the diene (3, R=Me). The diene 3, (R=Me; 600 mg) was dissolved in MeOH (25 ml) with 10% Pd-C (80 mg) and stirred under H_2 at room temp. and pressure until no further uptake of gas was observed. The soln was filtered and the solvent was removed *in vacuo* to yield an oil with identical glc retention time (5ft APL − 2% KOH at 90°) and IR and NMR-spectra to an authentic sample of 7, (R=Me).[6]

N-*Methyl-2-azabicyclo*[3.2.1]*oct-6-ene* (6, R=Me)

Method A. A soln of 6, (R=CO_2Me; 65 mg) in dry ether (17 ml) was added over 10 min to a stirred suspension of LAH (40 mg) in dry ether (30 ml) under N_2. The mixture was stirred at room temp. for 24 hr, and excess LAH was destroyed by careful addition of water. The soln was filtered and extracted with ether. The combined ether solns were dried (Na_2SO_4) and the solvent was removed *in vacuo* to yield an oil (40 mg, 84%) which was spectroscopically pure although thermally unstable, (Found: *m/e* 123.103661. $C_8H_{13}N$ requires; 123.104794); τ ($CDCl_3$ at −40°) 3.84 (1H, dxd, J 6Hz and 2Hz, H_6), 4.14 (1H, dxd, J 6Hz and 2Hz, H_7), 6.54 (1H, m, H_1), 7.30 (1H, dxd, J10 and 5Hz, *endo* H_3), 7.47 (1H, brs, H_5), 7.80 (1H, txd, J 10Hz and 5Hz, *exo* H_3), 7.83 (3H, s, NMe), 8.27 (m, H_{6n} + others), 8.40 (1H, d, J10Hz, H_{6x}), 8.70 (1H, m, H_4).

Method B. KOHaq (0.75 g in 20 ml H_2O) was added to a soln of 6, (R=H; 211 mg) in MeOH (20 ml). Me_2SO_4 (254 mg) was added to the mixture with ice cooling under N_2 and stirring was continued for 4 days at room temp. The mixture was extracted with $CHCl_3$ and the extracts were dried (Na_2SO_4). Removal of the solvent *in vacuo* yielded an oil, pure by glc, with identical spectra to the sample prepared by method A. The compound dimerised to an oil *m/e* 246 on standing at room temp.

N-*Methyl-2-azabicyclo*[3.2.1]*oct-3-ene* (8, R=Me). A soln of 8, (R=CO_2Me; 114 mg) in dry ether (10 ml) was added to a stirred suspension of LAH (120 mg) in dry ether (20 ml) and the reaction was stirred at room temp. under N_2 for 17 hr. Excess LAH was destroyed by careful addition of 2N aq KOH, ether was added and the ethereal layers were dried (Na_2SO_4). The solvent was removed *in vacuo* at 20° to yield a pale oil, (80 mg). This was very unstable dimerising even at −78°, *m/e* 246 (M^+, dimer) and several runs were required to obtain good spectra, τ ($CDCl_3$, −40°C) 4.47 (1H, d, J 7Hz, H_3), 5.47 (1H, txd, J 7Hz and 2Hz, H_4), 6.44 (1H, m, H_1), 6.71 (1H, m, H_5), 7.48 (3H, s, NMe), 7.67 − 8.10 (complex).

N-*Ethyl-2-azabicyclo*[3.2.1]*octa*-3, 6-*diene* (3, R=Et). A soln of anhyd ethylamine (45 mg) in dry benzene (2 ml) was added dropwise over 15 min to a suspension containing [2, (X=O)$\rightleftharpoons$1] (100 mg) and anhyd $MgSO_4$ (200 mg) in dry benzene (2.5 ml). The reaction was stirred at room temp. until the τ 0.84 doublet had gone from the ^1H NMR spectrum (*ca.* 0.5 hr). The soln was filtered and the solvent removed *in vacuo* to yield an oil (108 mg, 95%) (Found: *m/e* 135.104505. $C_9H_{13}N$ requires: 135.104794), $\nu_{max}^{CHCl_3}$ 1660 cm^{-1}, τ (CCl_4) 4.15 (1 H, dxd, J 6Hz and 2Hz, H_6), 4.58 (1H, d, J 7.5 Hz, H_3), 5.02 (1H, dxd, J 6Hz and 2.5Hz, H_7), 5.51 (1H, brt, J 7.5Hz, H_4), 6.22 (1H, brs, H_1), 6.69 (2H, q, CH_2CH_3), 7.58 (1H, m, H_5), 8.91 (3H, t, CH_2CH_3) for (3, R=Et) and absorptions at τ (CCl_4), 2.80 (1H, d, J 8Hz, imine), 4.22 (2H, brs, olefinic), 7.00 and 8.88 (2H and 3H, q + t, CH_2CH_3) for 2, (X=NEt). The diene form 3 was in excess, although, in $CDCl_3$, a similar spectrum was obtained except that the ratio 3, (R=Et) : 2, (X=NEt) was 2 : 3.

N-t-*Butyl-2-azabicyclo*[3.2.1]*octa*-3, 6-*diene* (3, R=t-Bu). t-Butylamine (135 mg) was added slowly to a suspension containg [2, (X=O)$\rightleftharpoons$] (200 mg) and anhyd $MgSO_3$ (400 mg) in benzene (3 ml) and the mixture was stirred at room temp. for 2.5 hr and filtered. The solvent was removed *in vacuo* to give an oil (260 mg, 81%), (Found: *m/e* 103.136009. $C_{11}H_{17}N$ requires: 103.136093); τ(CCl_4) 4.18 (1H, dxd, J 6Hz and 2.5Hz, H_6), 4.22 (1H, d, J 7Hz, H_3), 5.07 (1H, dxd, J 6Hz and 2.5Hz, H_7), 5.52 (1H, txd, J 7Hz and 2.5Hz, H_4), 5.83 (1H, brs, H_1), 7.48 (1H, m, H_5), 8.34 (1H, m, H_{6n}), 8.46 (1H, broad, H_{6x}), 8.61 (9H, s, CMe_3).

N-*tButyl-2-azabicyclo*[3.2.1]*octane* (7, R=tBu). A soln of 3, (R=Bu^t; 460 mg) in MeOH (25 ml) containing 10% Pd-C (185 mg) was stirred under H_2 at room temp. and pressure for 2 hr and filtered. The solvent was removed *in vacuo* to yield an oil (471 mg) which was a 1 : 1 mixture of isomeric amines by gc/ms. These were separated by preparative glc on 9ft 20% Apiezon–10% KOH at 140°C and the second fraction was a liquid (Found: *m/e* 167.167467, $C_{11}H_{21}N$ requires: 167.167391), τ (CCl_4) 6.57 (1H, brs, H_1), 7.24 (1H, dxd, J 6Hz and 10Hz, *endo* H_3), 7.57 (1H, txd, J 10Hz and 5Hz, *exo* H_3), 7.83 (1H, m, H_5), 8.41–8.80 (8H, complex), 8.97 (9H, s, CMe_3).

Treatment of the aldehyde [2, (X = O) $\rightleftharpoons$ 1] *with* H_2S *and acetylation of the product.* Gaseous H_2S and HCl were simultaneously passed into EtOH (40 ml) at 0° and a soln of [2, (X=O)$\rightleftharpoons$1] (500 mg) in EtOH (5 ml) was added dropwise over 10 min with stirring. Stirring was continued for 30 min at 0°, the gas supplies were disconnected and the mixture was diluted with $CHCl_3$ (100 ml) and washed with water. The organic layer was dried (Na_2SO_4) and the solvent was removed *in vacuo* to give an oil (300 mg) which was pure by tlc *m/e* 158 (M^+), ν_{max}^{film} 2505 cm^{-1} (SH), τ ($CDCl_3$) 4.37 (2H, s, olefinic), 5.46 (2H, m, H_1 and H_3), 6.78 (1H, m, H_5), 7.20–8.30 (5H, m). More concentrated solns gave a product with almost identical spectra but with *m/e* 282 (M^+).

The product (250 mg) was dissolved in anhyd pyridine (8 ml) with Ac_2O (2 ml) and left for 14 hr at room temp. The soln was added to water and extracted with $CHCl_3$. The extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo* to yield a product (138 mg) which was purified by preparative tlc (SiO_2: $CHCl_3$), *m/e* 200 (M^+), $\nu_{max}^{CHCl_3}$ 1689 cm^{-1} ($SCOCH_3$), τ ($CDCl_3$) 4.32 (2H, s, olefinics), 5.42 (2H, m, H_1 and H_3), 6.80 (1H, brm, H_5), 7.14–8.20 (5H, complex), 7.70 (3H, s, $COCH_3$).

2-*Thiabicyclo*[3.2.1]*oct-3-ene*(19). Compound 16[14,15] (57 mg) was dissolved MeOH (10 ml) with potassium azodicarboxylate (178 mg). AcOH (55 mg in 3 ml MeOH) was added to the ice-cooled suspension over 5 min under N_2 and stirring was continued for 1 hr at 0° and 2 hr at room temp. The solvent was removed *in vacuo* and the residue was extraced with $CHCl_3$. The extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo* to yield a yellow oil (38 mg, 65%) which was purified by tlc (SiO_2, hexane). The product was pure by glc (Found: *m/e* 126.050379. $C_7H_{10}S$ requires: 126.050320), τ ($CDCl_3$), 4.16 (2H, brd, olefinics), 6.79 (1H, m, H_1), 7.57 (1H, m, H_5), 7.70–7.80 (6H, complex m).

2-*Thiabicyclo*[3.2.1]*octane* (20). The diol 21[3] (2.0 g) in dry THF (20 ml) was added over 15 min to a stirred soln of PBr_3 (5.0 g) in dry ether (20 ml). Stirring was continued at room temp. for 16 hr and the mixture was added to 10% Na_2CO_3aq (25 ml) and extracted with ether. The extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo* to give an oil which distilled at 88–90° and 0.4 mm Hg (2.9 g 84%), pure by tlc (SiO_2:$CHCl_3$), *m/e* 177, 175 (M^+–Br), τ ($CDCl_3$) 5.84 (1H, m, H_1), 6.56 (2H, q, J 7Hz, H_7), 7.98 (5H, complex *m*). This dibromide (700 mg) was dissolved in EtOH with $Na_2S.9H_2O$ (1.2 g). The mixture was stirred at room temp. for 3 days and the solvent was removed *in vacuo*. The residue was diluted with water and the resulting suspension was extracted with $CHCl_3$. The extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo* to give a product which distilled at 85° and 8 mm Hg in a short path apparatus. The product (5%) was a colourless semi-solid identical in all respects with an authentic sample from Iranian kerosine oil.[16]

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